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Use of Reactive Oligomer to Improve Fracture Resistance of Epoxy Used in Medical Applications and GRP Pipelines

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Abstract: Epoxy is used as the polymeric matrix material in many medical and pipeline applications. As some examples this polymer is applied in fabrication of prostheses, dental applications, scaffolds, manufacturing glass reinforced pipelines (GRP) etc.. Herein, the toughness improvement of an epoxy resin was investigated systematically. For this purpose, we have utilized "Vinyl-terminated butadiene acrylonitrile (VTBN)" should be modified to "Vinyl butadiene (VB)" reactive oligomer that is known as a toughening agent for epoxy-based thermoset polymers. In order to evaluate the fracture resistance of the final composition, we have used several mechanical tests i.e. Fracture toughness test, Impact resistance test and unidirectional compression test. Moreover, in order to interpret the mechanical test data, damaged surfaces of fractured samples were investigated using scanning electron microscopy (SEM) techniques. It is found that VB improves fracture toughness of the epoxy resin more than twice. However this improvement fails by adding more than 25% VB. Moreover the impact strength of epoxy has been substantially improved. This is attributed to the high cavitations of VB particles. However, these improvements are accompanied with a slight reduction in compressive characteristics of modified samples. This is the result of low modulus of VB.

Key words: Epoxy resin · "Vinyl-terminated butadiene acrylonitrile (VTBN)" should be modified to "Vinyl butadiene (VB)" · Mechanical properties

INTRODUCTION

Polymer materials is frequently used in production of coatings, composites, medical applications and other advanced materials and structures [1-8]. Among the polymers, epoxy thermoset polymer is one of the interesting material for medicines and fluid conveying applications. This resin is chemically based on the epoxide group, a three-membered carbon, carbon, oxygen ring structure which is known as oxirane group [1]. The ability of this group to undergo a large variety of polymerisation and cross-linking reactions resuls in various types of resins with a wide range of chemical and physical properties, molecular weight and molecular structures. Epoxies are one of the most widely used adhesives for both structural and non-structural applications [1]. Epoxies have been used in a number of medical devices for bonding and sealing applications [1]. A clear, medical-grade low-viscosity epoxy adhesive has found application in fabrication of access ports that are implanted beneath the skin of patients requiring multiple injections. By allowing access for subsequent treatments, the access ports enhance patient comfort and reduce complications. In combination with a catheter assembly, access ports are used to deliver drugs to a particular area of the body. They can be used for arterial, venous, peritoneal or interspinal access [1]. The access port assembly is based on potting the stainless steel or titanium access port with an epoxy adhesive/encapsulant [1]. This particular adhesive passed biological and toxicity tests i.e. acute systemic and intracutaneous toxicity, implantation tests and cytotoxicity tests [1]. Use of epoxy resins in ultrasound catheters and pacemakers are the typical examples of its use in medical electronic packages [1]. Certain types of medical-grade epoxy adhesives are also capable of being sterilized by autoclave and chemical

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methods [1]. These types of epoxy resins could be used in medical devices that require sterilization prior to its use [1]. A silver-filled epoxy has been used for bonding critical components in hybrid circuits within pacemakers [1]. Epoxies are also being used for joining filter components. Another application of epoxy in medicine is the use of a two- part epoxy for bonding end-caps to the main tube of a blood filter [1].

However it should be noted that the epoxy polymer is highly brittle. Indeed this thermoset material exhibits very low impact strength and fracture resistance. Therefore several methods are used by engineers and manufacturers for enhancing the strength of epoxy to prevent failure and critical damages. It is well-established that rubber modification that is the addition of rubber particulate phase to a brittle polymer, is one of the most successful approaches for improving toughness of epoxy. Reactive oligomers can be used as rubber modifiers for toughening of epoxy. Rubber modification of epoxy has been studied by previous researchers. Ophir *et al*. [9] investigated a modified epoxy composition for filament winding of pressure vessels. Their product showed an improved toughness with minimal sacrifice of its thermal and mechanical properties. Zhang *et al*. [10] used carboxyl-terminated butadiene acrylonitrile (CTBN) to modify the toughness of reinforced epoxy tubes. They found that the ultimate strain was higher for the toughened pipes [10]. Sanjana *et al*. [11] reported that the toughness improvement of epoxy composites is affected by physical conditions as well as modifier type. Abadyan *et al*. [12] observed that addition of amine-terminated butadiene acrylonitrile (ATBN) to epoxy matrix increases impact strength of modified hoop wound composite but reduces its compressive and interlaminar shear strength. Moreover incorporation of ATBN led to more favorable mechanical properties, from the viewpoint of both toughness and strength, relative to CTBN [13]. Other researchers reported that the incomplete precipitation of oligomer molecules might enhance the toughness characteristics and decrease the other mechanical characteristics of a modified resin [14]. Moreover, in Ref. [15] it has been shown that the increasing in the loading rate of epoxy samples might lead to reduce the damage zone in the vicinity of the crack tips. This reference shows that cavitation has a great influence on the fracture toughness of epoxy matrix. In other works, the incorporation of two types of rubber modifier on fracture toughness of epoxy has been examined [16-18]. The researchers reported a synergistic toughening in fracture toughness of epoxy modified by a combination of reactive oligomer and waste tire particles [16-18].

Table 1: Formulations made in this study

Sample code	Resin (phr)	Hardener (phr)	Modifier type	Modifier Content (phr)
N	100	38	-	0
V5	100	38	Hycar 2000*168	5
V10	100	38	Hycar 2000*168	10
V15	100	38	Hycar 2000*168	15
V20	100	38	Hycar 2000*168	20

There is still lack of knowledge on the effect of modifiers on mechanical characteristics of epoxy polymer. In this regards, "Vinyle-terminated butadiene acrylonitrile (VTBN)" should be modified to "Vinyl butadiene (VB)" oligomer is utilized to modify the epoxy in this work. Various kinds of physical and mechanical tests and microscopic techniques are conducted in this study.

Experimental

Materials: The model system used in this study is based on a diglycidyle ether of bisphenol A epoxy. The trade name of the material is Araldite LY5052 from Hauntsman Co. The hardener part is a cycloaliphatic polyamine hardener with the trade name of HY5052 from Vantico. The liquid modifier is "Vinyl-terminated butadiene acrylonitrile (VTBN)" should be modified to "Vinyl butadiene (VB)" copolymer with the trade name of Hycar1300×33 from Novion Co. This type of modifier has no acrylonitrile content.

Sample Preparation: The stoichiometric ratio of the resin and hardener were mixed and degassed at room temperature for 20 min. Then it was casted in a mould and was cured for 8h at 80°C in an oven. Same curing procedure was employed for all toughened epoxies. The modifier content was varied up to 20 phr. The obtained mixtures were mixed under vacuum for 20 min. Table 1 presents the epoxy formulations used.

Characterization Techniques

Resin Evaluation: Compressive characteristics of epoxy resin were determined according to ASTM D695 using a computer controlled Hunsfield testing frame. Samples were prepared by machining the cast sheet. Plane strain fracture toughness, K_{IC}, was measured using SEN specimens tested in 3PB loading condition. Specimens with 5 mm thickness were prepared for this experiment according to ASTM D5045 guideline. Plane strain fracture toughness, K_{IC}, was determined using single-edge-notch (SEN) specimens tested in three-point-bending (3PB) geometry. The ASTM D5045 guideline was followed to measure K_{IC}. Pre-cracks were introduced at the bottom of 2-mm deep notches by hammering a razor blade which was chilled in liquid nitrogen. An impact test was

accomplished according to ASTM D 256 using standard notched specimens. Samples were prepared and machined to the standard shape. Samples were tested using an 1 J hammer energy.

Microscopy Evaluation: The surfaces of the K_{IC} specimens were examined using scanning electron microscope (SEM). In order to produce a conductive surface the fractured surface of samples were first coated with a thin layer of gold. SEM samples were coated with a thin layer of gold before examination to protect the fracture surfaces from beam damage and also to prevent charge build up.

RESULTS AND DISCUSSION

Compressive Properties: Since the compressive characteristics plays an important role in mechanical performance of polymer-made materials especially in high-temperature applications, we firstly investigated this issue systematically. Table 2 demonstrates the compressive strength of epoxy resin as a function of oligomer content. The compressive strength gradually decrease with increasing Hycar 2000*168 content (Table 2). This is the result of the lower strength of oligomer in comparison with the epoxy. Reduction of the macroscopic yield stress can lead to increase in fracture toughness [11]. Oligomers affect mechanical properties of epoxy depending on their chemical structure and content [12].

Table 3 demonstrates the compressive elastic modulus of epoxy resin as a function of oligomer content. Similar to what observed in the case of compressive strength, the compressive modulus gradually decrease with increasing Hycar 2000*168 content. This is the result of the lower modulus of oligomer in comparison with the epoxy. Note that rubbery and elastomer materials usually have a lower strength and modulus than those of thermoset resins.

Table 2: Compressive strength of resin

Sample	Compressive Strength (Mpa)
N	81
V5	79
V10	76
V15	74
V20	67

Table 3: Compressive modulus of resin

Sample	Compressive Modulus (Gpa)
N	2.9
V5	2.8
V10	2.8
V15	2.6
V20	2.4

Table 4: Fracture toughness of resin

Sample	K_{IC} (Mpa.m$^{0.5}$)
N	0.7
V5	1.9
V10	2.2
V15	2.3
V20	1.6

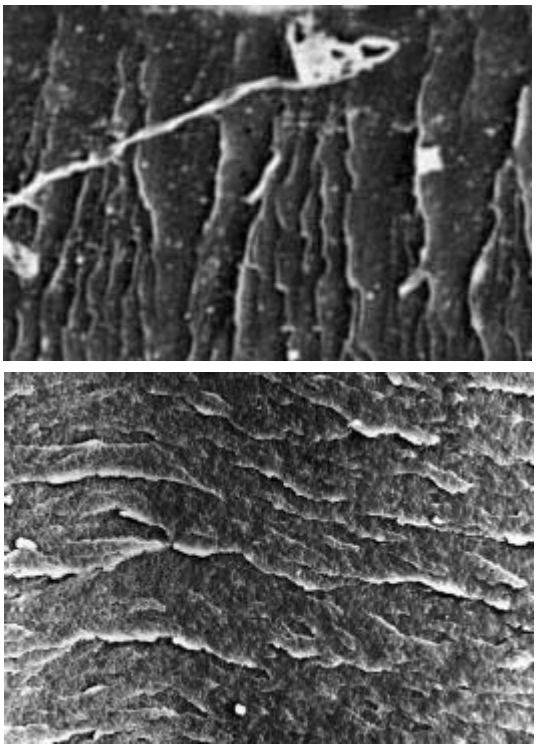

Fig. 1: SEM micrographs from the fracture surface of specimens: (a) N, (b) V10.

Fracture Toughness: It is well-established that oligomers usually can improve the fracture toughness of brittle epoxies. Reactive oligomers can be used as rubber modifiers for toughening of epoxy. The results of fracture to ughness measurements are listed in Table 4. As seen, oligomer increases fracture toughness of resin. As seen the fracture toughness of modified epoxy increases up to 15 phr modifier content. However, more rubber addition cannot be useful since the fracture toughness of the samples decreases beyond the 15 phr VB content (see sample V20 for example). This reveals there are an optimum value of modifier for improvement of epoxy. This should be considered by engineers to produce a reliable toughened epoxy.

Figure 1 shows the SEM images has been taken from the fracture surfaces of N and V10 samples. Figure 1(a) corresponds to the surface of unmodified sample (N) and figure 1(b) corresponds to the fracture surface of

Table 5: Impact resistance of resin

Sample	I_{imp} (kJ/m^2)
N	3.25
V5	5.05
V10	6.34
V15	7.16
V20	5.31

VB-modified (V10) sample. The flat pattern seen in Figure 1(a) indicates the brittle fracture of neat epoxy (N sample). No evidences of massive plastic deformation can be observed in the flat surface. However, the rough pattern of V10 surface seen in Figure 1(b). The rough pattern is an indicative of massive deformation and cavitation on the fracture surface of modified samples. This shows the significant amount of deformation in the modified sample (V10 sample) that is the result of stress concentration and concomitant cavitation of VB particles. Note that cavitation plays an important role in toughening and increasing the toughness of rubber-modified epoxies. Cavitation is one of the most important mechanisms in rubber modification that occurs in the vicinity of crack tip. Previous researchers investigated toughening mechanisms in CTBN and ATBN rubber toughened epoxies and showed that cavitation is a prerequisite for massive shear deformation of the matrix. The latter is known as the main source of energy absorption in fracture of rubber toughened epoxies.

Impact Strength Evaluation: Impact strength is known as a rough criterion for evaluating the toughness of a material. While it might be not accepted as a scientific data in scientific researches, however this produces a good physical interpretation of the toughness for engineers and designers. The impact strength (I_{imp}) of VB-modified epoxy samples are measured and listed in Table 5. Increase in impact strength is reported in samples containing VB oligomer. Increasing modifier content leads to an increasing in impact strength. The normalized value of impact strength is listed in Table 6. This table reveals the amount of effect of modification on impact resistance of material. As seen by addition of 15 phr VB one can increase more than % in impact resistance of the material. This is the result of inducing cavitation and massive shear yielding in the epoxy matrix due to the stress concentration of VB particles [15]. This mechanism is similar to what metioned abut the fracture toughness test and isknown as the dominat mechanism for energy absorption in modified epoxies.

An interesting point is that previous researches reveals less cavitation and void grows in the case of the impact test specimen compared to fracture toughness test samples. Decrease in cavitation and void growth corresponds to decrease in plastic deformation and energy absorption. It is the result of higher loading rate of impact test in comparison with fracture toughness test. Previous research showed that at high loading rate, toughening mechanisms such as cavitation and void growth are suppressed [15].

CONCLUSIONS

In this paper a liquid oligomer was employed as toughening agents in epoxy. We have used mechanical tests including fracture toughness (K_{IC}) test, Impact strength test and unidirectional compression test (σ_{uc}). Moreover, in order to interpret the mechanical test data, damaged surfaces of fractured samples were investigated using scanning electron microscopy (SEM) techniques. It is found that the mode I fracture toughness of resin increased by oligomer modification. Results showed that VB improves fracture toughness of the epoxy resin more than twice. However this improvement fails by adding more than 25% VB. Moreover the impact strength of epoxy has been substantially improved. This is attributed to the high cavitations of VB particles. However, these improvements are accompanied with a slight reduction in compressive characteristics of modified samples. This reduction in other mechanical properties such as compressive characteristics is the result of low modulus of VB particles. SEM fractography reveals that oligomers precipitate from the epoxy matrix which effectively increases epoxy toughness. The higher toughness characteristics of the VB-modified epoxy can be interpreted via considering the cavitation of VB particles in the matrix.

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